CWIP

Coastal Water Quality Monitoring Program
An Assessment of the Quality Control Component

ARD

Coastal Water Quality Improvement Project

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Coastal Water Quality Monitoring Program
An Assessment of the Quality Control Component

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Government of Jamaica's
Natural Resources Conservation Authority

And the

United States Agency for International Development

Implemented by:

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PREFACE

The Coastal Water Quality Improvement Project (CWIP) is a six-year bilateral initiative between the Government of Jamaica's Natural Resources Conservation Authority (NRCA) and the United States Agency for International Development (USAID). Five distinct, but interrelated, activities associated with coastal water quality improvement are being carried out to form a synergy of interventions contributing to the achievement of the USAID Strategic Objective 2 (SO2) – Improved quality of key natural resources in selected areas that are both environmentally and economically significant. CWIP is being implemented by Associates in Rural Development, Inc. (ARD) with assistance from Camp, Dresser & McKee, Inc. (CDM) and the Construction Resource and Development Centre (CRDC).

The objective of this report is to present and describe the findings of the inter laboratory comparison and other quality assurance components of the water quality monitoring exercise in order to address issues concerning data validity, and to identify areas within the program that need refinement toward generating results that are defensible.

This report is prepared by Dr. Anthony Greenaway, Senior Lecturer in the Department of Chemistry at the University of the West Indies (UWI), with the data that was available for analysis during the fifteen month period under review. Dr. Greenaway is also an Associate of the UWI's Centre for Marine Sciences (CMS), serves as Chairman of the subcommittee on Quality Management Systems of the Jamaica Bureau of Standards writing standards for laboratory accreditation, and is an Advisor to the Coastal Water Quality Monitoring component of CWIP.

The data contained therein, describes only the Negril program at this time. Negril represents the first Project site where the Pilot Program was initiated.

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ACRONYMS

ARD	Associates in Rural Development, Inc.
CDM	Camp, Dresser & McKee, Inc.
CMS	Centre for Marine Sciences
CRDC	Construction Resource and Development Centre
CWIP	Coastal Water Quality Improvement Project
DBML-CAF	Discovery Bay Marine Laboratory Chemical Analytical Facility
NEPT	Negril Environmental Protection Agency
NRCA	Natural Resources Conservation Authority
NRCA	Natural Resources Conservation Authority
NWC	National Water Commission
SO2	Strategic Objective 2
USAID	United States Agency for International Development
UWI	University of the West Indies

INTRODUCTION

The Coastal Water Quality Monitoring Program in Negril has now been running for 15 months. Seven sampling trips have been effected, the data for the first six being presently available. Trips have been on December 1, 1998, February 11, June 1, August 11, October 27 and December 8, 1999 and February 14, 2000. Sixteen sites are being sampled on each trip.

The quality control procedures consist of 2 components:

a) analyses of collected duplicate samples, and
b) the analyses of inter-laboratory comparison samples.

Participating laboratories are expected to have their own quality control procedures.

Nutrient samples were analysed at the Discovery Bay Marine Laboratory Chemical Analytical Facility (DBML-CAF). The coliform samples were analysed at the Ministry of Health's Kingston laboratory by an analyst from the Natural Resources Conservation Authority's (NRCA) Kingston laboratory. All nutrient and coliform inter-comparison samples were analysed at the Montego Bay Laboratory of the National Water Commission (NWC).

The data considered in this report are presented in Appendices 1 (paired duplicates) and 2 (inter-comparison data).

RESULTS AND INTERPRETATION

a) Duplicates

At four of the sixteen sites, duplicate samples were collected. The samplers drew bottles at random and whereas the laboratory analysts were informed of the bottle numbers but they had no information linking bottle numbers to sites for which bottles represented duplicate samples. Laboratories submitted their results against bottle numbers and the program coordinator linked the results back to the sites. Twenty-five (25) sets of duplicates were collected from the six trips for which data are available. (On 1 trip a 5^{th} duplicate were inadvertently collected.)

The variabilities within these duplicates were treated by the method of paired duplicates (standard deviation = square root of $\{[\sum(d_1-d_2)*(d_1-d_2)]/2n\}$ where d_1 and d_2 are the results for the pairs and n is the number of duplicates included in the calculation. The summation was done over all pairs (J.K. Taylor, 1986, Quality Assurance of Chemical Methods, Lewis Publishers).

The DBML-CAF determined salinities by refraction on all samples that were received. If the salinity varied within a pair this could mean either errors in the salinity measurements or that the duplicate pair did not represent a homogeneous pair. The latter is distinctly possible for samples from the rivers where fresh waters overlie saline waters. Only twice were the salinities significantly different within a pair (February 11: 35 vs 17, and December 8, 1999: 33 vs 26). For neither of these pairs were the duplicate differences (d_1-d_2) for other parameters greater than found for pairs when the salinities agreed. It is assumed therefore that within the uncertainties to be documented below, all duplicates represented sampling from homogeneous water bodies.

Table 1 summarizes the results of the standard deviation calculations. For each parameter, the data were sorted into ranges to ensure that no pair dominated the standard deviation calculation. Some pairs were omitted from the standard deviation calculations. The relevant laboratories should be asked to consider these points again. These are listed in the last column of Table 1. The entire data set is given in the Appendix 1. The parameters will be considered in turn.

Chlorophyll-a *(DBML-CAF data)*

Only two pairs are considered to be deviant and thus 96% of ***the data can be considered satisfactory and the coefficient of variation for the data lies somewhere between 10 and 25%*** with the 25% being relevant to data close to the detection limit.

Total Suspended Solids *(DBML-CAF data)*

In both ranges the uncertainties are of the order of 10-30% and most often at the lower end of that range. ***The data can be considered satisfactory with an appropriate coefficient of variation of the order of 15-20%.***

Total Dissolved Phosphorus *(DBML-CAF data)*

The 31.4 & 34.5 pair show tolerable agreement. ***All data are satisfactory although the variability within the 1 -5 range, being of the order of 20-100%, is higher than ideal. The laboratory should be asked to consider ways to reduce this.***

Dissolved Inorganic Phosphorus *(DBML-CAF data)*

Five pairs or 20% of the data are considered to be outside the acceptable variability. The concentrations within the 2 pairs in the greater than 3 range differ by only 10-15% and are therefore acceptable. ***Thus only 80% of the data are satisfactory and a coefficient of variation of 10 and 20% would apply to them***, the upper value corresponding to values close to the detection limit. ***The laboratory should be asked to consider how they can move towards a higher % of acceptable data***.

Nitrate plus Nitrite *(DBML-CAF data)*

Five data pairs show greater variability than that considered to be reasonable. ***A coefficient of variation of approximately 10-15% applies to majority of the acceptable data but only 80% of the data fall into that category. The laboratory should be asked to consider how they can move towards a higher % of acceptable data***.

Total Dissolved Nitrogen *(DBML-CAF data)*

Four of twenty-five pairs are unacceptable. ***The 84% of the data which show acceptable variability have a coefficient of variation of about 10-20%.*** The big differences within the unacceptable pairs needs investigation.

Ammonia *(DBML-CAF data)*
The 84% acceptable data have coefficients of variation of between 5 and 15%.
pH *(DBML-CAF data)*

The pH values varied between 7.5 and 8.4 with pairs agreeing to within 0.1 pH units. All data are satisfactory.

Faecal Coliforms *(NRCA data)*

Of the 16 pairs of data available 7 have both points less than 100 while 1 has both points greater than 1600. Of the 7 pairs in the 200-1000 range 4 have one point less than 100 and the other greater than 200. ***The uncertainty in the 200 - 1000MPN range (45% of the data) is high (25-100%) and thus makes decisions concerning the 200MPN action limit difficult.*** The laboratory should seek ways to reduce the variability.

b) Inter-Laboratory Comparison Data

The NWC's Montego Bay (nutrients and coliforms) and the DBML-CAF (nutrients) and NRCA (coliforms) laboratories were involved in this exercise. For the first three field trips the inter-comparison exercise required the NWC staff to collect their samples in their own bottles along side the community volunteers whose bottles were supplied by the DBML-CAF (nutrients) and NRCA (coliforms). The NWC staff collected samples from most of the 16 sites on those trips. Those inter-comparisons therefore included bottle preparation, sampling, transport, analytical and reporting components. The NWC have forwarded data (total phosphorus, phosphate, nitrate plus nitrite, and feacal coliforms) for the June trip only.

For the subsequent trips the bottles were supplied by the DBML-CAF and sites were designated at which the community samplers were to collect samples for the NWC, the change aimed at limiting the comparison to analytical and report writing. Five sites were designated each trip, one of which was a duplicate site. In addition, the NWC continued to sample at most sites with their own bottles. No data were forwarded for the samples collected by the community samplers. The only data available for consideration were data which reflected bottle preparation, sampling transport, analysis and reporting factors.

NWC data were forwarded as follows:

August 99 - Total suspended solids.

October 99 - Total suspended solids and feacal coliforms.

December 99 - Total phosphorus, phosphate, nitrate and nitrite, feacal coliforms and total suspended solids.

The data presented are given in Appendix 2.

The NWC had expressed limited confidence in their December data. However those data show similar comparison patterns as the June data and thus were included in the following assessments. The nutrient data were supplied in mg(N or P)/L and so have been converted to units of µmols/L by multiplying by 1000/31 (for P) or 1000/14 (for N).

The parameters will be considered in turn.

Total Dissolved Phosphorus

The June 99 data for the two laboratories bear no resemblance. The NWC data are between 6 and 200 times larger than the DBML-CAF data. The December 99 data show a rough correlation (DBML-CAF = 0.1*NWC + 0.45; R^2 = 0.8) but neither the slope nor the intercept are acceptable.

Dissolved Inorganic Phosphorus

The June 99 data for the two laboratories bare no resemblance. The NWC data are generally between 6 and 150 times bigger than the DBML-CAF data. A reasonable correlation exists for the December 99 data (DBML-CAF = 0.36*NWC + 0.14; R2 = 0.97 when one pair (30.2/4.7 NWC/DBML-CAF) is omitted). This correlation however is unacceptable as the coastal waters are expected to have inorganic phosphorus concentrations less that the regression's intercept. The slope should be 1.

Nitrate Plus Nitrite

If all data are included a rough correlation exists (DBML-CAF = 1.04*NWC + 1.2; R^2 = 0.73) but the intercept is well above the expected marine concentrations. No interpretive improvement results from excluding the 3 significant outliers (22/57, 21.7/1.2 and 41/58) from the correlation (DBML-CAF = 0.86*NWC + 0.5; R^2 = 0.998). The December 99 data show similar disagreement.

Total Suspended Solids

For all three sets (August 99, October 99 and December 99) the DBML-CAF data for the marine sites are of the order of 20 while the NWC data show more variability but generally are 2 - 5 times smaller. The river site data from the DBML-CAF are generally at least twice those of the NWC. There is no acceptable agreement between the laboratories.

Feacal Coliforms

In both October and December 99 the agreement between the NWC and the NRCA was similar to the agreement for duplicates within the NRCA laboratory (see above).

The laboratory inter-comparison program has not been working satisfactorily. For nutrients it is clear that there is limited if any agreement between the NWC and DBML-CAF. Before any significant decisions can be made the data compiled for this report should be returned to the laboratories for checking. Once checked the laboratory managers and the analysts should meet to consider the data. ***For coliforms the laboratories are somewhat more in agreement but internal variability is higher than desired (see above consideration of duplicates).*** In future all inter-comparison data must be cross checked by the laboratories before any data are released to the community. In the January 2000 Ocho Rios and February 2000 Negril trips the sampling for inter-comparison purposes was under control and hopefully will produce data that can be seriously considered.

RECOMMENDATIONS

a) The coefficients of variation for the parameters, as calculated from the paired duplicates, are generally at about 20% or less, which is not unsuitable for this program. However the laboratories should attempt to improve their precisions, especially for the lower concentrations.

b) In future the duplicate data must be returned to the labs for confirmation as quickly as possible and then their appropriateness should be assessed prior to disseminating the data.

c) The laboratory inter-comparison exercise must be brought under control. At this stage the involved laboratory personnel should be brought to a meeting to discuss sampling procedures, analytical methods and possible areas of divergence. Visits between labs by analysts to allow them to observe procedures may also help.

d) The sampling procedures as carried out during the last Negril and the first Ocho Rios trips should be accepted as the standard procedure for the coastal Water Quality Monitoring Programs. The community samplers under the supervision of the Project Coordinator must be responsible for the collection and dispatching of the laboratory inter-comparison samples. The attached "Instructions to Samplers" and "Instructions to NEPT" which were used in Negril in February 2000 define the procedures.

e) Data dissemination should be as follows: After sampling, the Project Coordinator (NEPT in Negril, DBML in Ocho Rios) should dispatch the samples and "Chain of Custody Forms" to the appropriate laboratories. The laboratories should complete the analyses and then send the data along with the completed "Chain of Custody Form" to the relevant Project Coordinator. The data should be submitted in electronic form (an excel spreadsheet) and in hard copy. The Project Coordinator will on the spreadsheet link the site numbers to the bottle numbers and then return the data (hard and electronic copies) to the relevant laboratories for cross checking and duplicate data considerations. Once satisfied that the data are correct the laboratories will return the data, amended if necessary (both electronic and hard copies), to the Project Coordinator who will then consider the duplicate and inter-comparison data. If satisfied (s)he will prepare the data for dissemination to the community. If not satisfied (s)he will consult the laboratories in order to decide as to how to proceed.

Table 1: A Summary of the Paired Duplicate results.

Parameter	Detect. Limit	Ranges	Number of Pairs	Standard Deviation	Omitted pairs
Chlorophyll-a mg/m^3	2	2-4	17	0.5	38 & 63 4 & 96
		5-34	6	3	
`Total Suspended Solids; mg/L	5	5-30	11	3	18 & 51 18 & 49
		31-120	12	9	
Total dissolved Phosphorus; µM	0.06	0.1 – 1	18	0.1	
		1.1 – 5	6	1	
		> 30	1	See text	
Dissolved Inorganic Phosphorus; µM	0.02	0.02 - 0.1	9	0.02	0.06 & 0.23 0.08 & 0.27 0.19 & 0.71 0.48 & 1.0 0.57 & 1.05
		0.1 - 1.6	9	0.1	
		3 – 22	2	See text	
Nitrate plus nitrite; µM	0.1	0.1 - 1.6	9	0.1	0.6 & 1.5 0.62 & 1.2 0.64 & 9.29 4.4 & 14.5 18.4 & 33.1
		2.5 – 11	6	1.2	
		11 – 59	5	2	

Parameter	Detect. Limit	Ranges	Number of Pairs	Standard Deviation	Omitted pairs
Total Dissolved Nitrogen µM	0.5	0.5 - 4.1	12	0.9	1.1 & 14.5 2.7 & 10.8 6.8 & 65.9 32 & 55
		4 – 15	6	0.8	
		15 – 56	3	4.4	
Ammonia µM	0.3	0.3 – 1	11	0.1	0.6 & 1.4 0.6 & 1.5 1.6 & 2.7 6.6 & 16.6
		1 – 14	10	0.3	
Faecal Coliform	2	2 – 100	7	20	240 & 1600
		200 – 1000	7	260	
		> 1600	1		

Appendix 1: Paired Duplicates

Nitrate Plus Nitrite det lim = 0.1 uM sample 1	sample 2	Ammonia det lim = 0.3 uM sample 1	sample 2	Total Dissolved Nitrogen det lim = 0.5 uM sample 1	sample 2
0.03	0.03	0.2	0.2	0.4	3.1
0.10	0.40	0.2	0.2	0.4	1.7
0.20	0.50	0.2	0.3	1.1	14.5
0.30	0.40	0.2	0.2	1.8	2.4
0.50	0.60	0.2	0.2	1.9	2.5
0.60	1.50	0.2	0.6	2.0	2.3
0.62	1.20	0.3	0.7	2.1	4.3
0.64	9.29	0.4	0.4	2.4	2.5
0.90	1.00	0.4	0.6	2.7	10.8
1.00	1.00	0.5	0.5	2.8	3.8
1.10	1.30	0.6	1.4	3.0	5.0
1.50	1.64	0.6	1.5	3.3	4.6
2.50	2.86	0.9	1.1	3.4	3.6
2.60	3.00	1.0	1.7	4	4.1
3.00	5.29	1.0	1.1	4.3	6.6
4.29	6.43	1.0	1.6	5.7	6.5
4.40	14.50	1.1	1.3	6.8	65.9
6.40	8.30	1.1	1.5	9.0	9.8
9.29	11.43	1.3	1.5	9.3	10.0
10.71	12.41	1.6	2.7	10.4	10.4
12.50	12.70	2.8	2.8	13.9	15.0
15.00	17.00	3.6	3.6	14	21
18.00	24.00	6.6	16.6	17	26
18.40	33.10	6.8	7.4	32	55
57.00	59.00	14.0	14.0	51.0	56.0

Appendix 1: Cont'd

Dissolved Inorganic Phosphorus		Total Dissolved Phosphorus		Total Suspended Solids	
det lim =	**0.02 uM**	**det lim =**	**0.06 uM**	**det lim =**	**5 mg/L**
sample 1	sample 2	sample 1	sample 2	sample 1	sample 2
0.02	0.02	0.1	0.2	3	11
0.02	0.09	0.1	0.2	7	15
0.02	0.02	0.1	0.3	13	14
0.03	0.05	0.1	0.4	13	15
0.03	0.04	0.1	0.5	18	51
0.03	0.08	0.2	0.2	18	18
0.06	0.23	0.2	0.2	20	22
0.08	0.08	0.2	0.4	23	22
0.08	0.11	0.3	0.3	27	23
0.08	0.27	0.3	0.3	28	27
0.09	0.10	0.3	0.3	29	26
0.16	0.19	0.3	0.3	29	22
0.19	0.71	0.3	0.7	31	32
0.26	0.26	0.3	0.4	31	42
0.35	0.39	0.4	0.6	34	29
0.39	0.39	0.4	0.5	39	50
0.42	0.51	0.5	0.6	44	57
0.48	1.00	0.8	1.0	46	48
0.55	0.66	1.1	2.4	49	18
0.57	1.05	1.2	3.5	51	25
0.61	0.65	1.2	1.3	55	26
0.90	1.25	1.9	3.4	68	80
1.40	1.60	2.5	3.0	78	81
2.71	3.26	2.9	5.2	110	115
19.10	22.10	31.4	34.5	116	121

Appendix 1: Cont'd

Chlorophyll-a		**salinity**		**Faecal coliforms**	
det lim =	**2 mg/m3**	**det lim =**	**5**	**det lim =**	**2 MPN**
sample 1	sample 2	sample 1	sample 2	sample 1	sample 2
2	2.1	3	3	2	2
2	2	3	3	2	2
2	2	5	6	2	2
2	2.4	5	5	2	2
2	3	9	9.5	2	12
2	2	15	15	6	80
2	2	16	13.5	18	49
2	2	16	18	23	500
2	4	33	25.5	26	240
2	2	33.5	35	27	280
2	2	35	35	170	240
2	2	35	35	170	500
2	2	35	35	220	2
2	3	35	35	240	900
2.1	2.2	35	35	240	1600
2.1	2.2	35	35	1600	1600
3.2	3.8	35	35		
4	96	35	35		
5.5	8.4	35	17		
6.1	8.8	35	36		
7	12	36	35		
13	17				
28	36				
32	34				
38	63				

Appendix 1: Cont'd

pH

sample 1	Sample 2
7.5	7.6
7.6	7.5
7.6	7.7
7.7	7.9
7.7	7.8
7.7	7.75
7.7	7.9
7.8	7.7
7.9	7.7
8	8
8	8.1
8.1	8.1
8.1	8.1
8.1	8.1
8.1	8.1
8.1	8.1
8.1	7.9
8.2	8.3
8.2	8.2
8.2	8
8.2	8.1
8.2	8.15
8.3	8.3
8.35	8.3
8.35	8.35

Appendix 2: Laboratory Inter-Comparison Data

Jun-99 site	Total Dissolved Phosphorus uM		Dissolved Inorganic Phosphorus uM		Nitrate plus Nitrite uM		Total Suspended Solids mg/L		Faecal Coliforms MPN	
	NWC	DBML	NWC	DBML	NWC	DBML	NWC	DBML	NWC	NRCA
1	9.10	2.20	0.35	1.30	62.16	54			200	500
2	94.42	2.50	58.94	1.50	22.08	57			540	240
3	44.74	3.30	27.39	1.60	41.22	58			170	500
4	73.81	0.30	20.00	0.12	21.68	1.2			2400	1600
5	3.77	0.30	0.65	0.11	0.48	0.9			2	1
6	3.90	0.30	0.77	0.10	0.61	0.8			2	1
7	7.03	0.30	0.90	0.11	0.32	1.6			2	1
8	2.13	0.30	1.03	0.10	0.55	1			2	1
9	2.00	0.30	0.61	0.10	0.55	0.9			2	1
10	1.87	0.30	1.45	0.12	0.82	1.3			2	1
11	22.45	0.20	1.87	0.05	0.50	0.4			2	4
12	3.35	0.20	0.35	0.20	0.37	0.03			2	2
13	14.16	0.30	2.55	0.07	0.32	0.9			2	13
14	11.39	0.90	2.13	0.42	8.98	10.1			5400	1600
15	7.71	1.20	0.35	0.60	15.87	12.6			540	700
Dec-99										
1										
2	41.94	8.10	12.35	4.6	215.07	180	8	51	500	170
3	85.48	7.80	30.23	4.7	127.43	180	23	51	330	23
4	24.84	2.10	2.10	0.88	24.14	46	13	52	5400	110
5	1.71	0.10	0.13	0.03	31.14	0.2	1	19	5	2
6										
7	3.52	0.20	0.13	0.06	3.00	0.4	2	17		
8										
9	2.87	0.10	0.13	0.03	2.14	0.1	4	49	7	23
10	0.71	0.10	0.26	0.04	2.29	0.3	3	20		
11	1.97	0.90	0.26	0.46	0.29	16	3	19		
12	1.55	0.90	0.13	0.49	1.71	18	3	17	8	7
13	3.52	0.20	0.52	0.05	2.07	0.5	5	18		
14	1.84	0.60	0.39	0.31	29.71	11	9	54	920	1600
15	3.84	2.00	0.65	0.77	66.57	20	15	57	3500	220

	16									920	350

Appendix 2: Cont'd

Aug-99 site	Total Dissolved Phosphorus uM		Dissolved Inorganic Phosphorus uM		Nitrate plus Nitrite uM		Total Suspended Solids mg/L		Faecal Coliforms MPN	
	NWC	DBML	NWC	DBML	NWC	DBML	NWC	DBML	NWC	NRCA
1							22	44		
2							29	52		
3							31	120		
4							33	30		
5							1	13		
6							45	12		
7							4	12		
8							4	12		
9							7	14		
10							7	18		
11							7	13		
12							20	16		
13							3	13		
14							17	322		
15							19	32		
Oct-99										
1							12	50	14000	900
2							10	44	7900	1600
3							78	111	13000	1600
4							6	55	1700	1600
5							50	21	2	13
6									2	2
7							6	23	2	2
8							19	22	2	2
9							10	21	2	2
10							1	22	2	2
11							1	21	2	2
12							8	24	540	2
13							23	24	8	2
14							22	46	490	570
15									90	300

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